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Single pulse threshold and transmission behaviour of a triazeno-polymer during pulsed UV-laser irradiation

T. Lippert [a,*], L.S. Bennett [b], T. Nakamura [a], H. Niino [a], A. Yabe [a]

[a] Laser Induced Reaction Laboratory, National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan
[b] Energetic Materials Laboratory, National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan

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Abstract

The threshold fluence F_{Th} of a triazeno-polymer was measured in the low fluence range for thin films using conventional UV-spectroscopy. It was found that there is a clearly defined F_{Th} for 308 nm irradiation between 20 and 25 mJ cm^{-2}. In the case of 248 nm irradiation, a 'threshold fluence range' between 16 and 32 mJ cm^{-2} was determined. Additional transmission measurements have been performed showing that the target transmission at 248 nm increases only slightly, whereas for 308 nm the transmission increases by a factor of ≈ 4. This result shows that dynamic target absorption properties are very important for describing the ablation process.

1. Introduction

Since the very first reports about etching of organic polymers [1,2] using pulsed UV lasers, numerous studies [3,4] were published and applications including surgery [5–8] and image transfer [9,10] have been found.

In previous studies [11,12], the development of a novel class of photopolymers designed for ablation at 308 nm have been described. These investigations show that the concept of designing polymers for laser ablation at specific wavelengths is feasible. The ablation at 308 nm resulted in high resolution etching of one chosen polymer.

In spite of the higher extinction coefficient in solution, the polymer showed a higher ablation rate at 308 nm as compared to 248 nm. For an understanding of these unexpected results, different aspects of the photoablation process must be considered. In recent studies, attention was drawn to the absorption properties of the polymer during the laser pulse [13,14]. These results were analysed theoretically using a two-level model of chromophore absorption [15].

In this paper, thin polymer films of one selected triazeno-polymer (structure shown in Scheme 1) were chosen to study the low fluence range irradiation behaviour and the fluence dependent transmission during the pulsed laser irradiation.

2. Experimental methods

2.1. Material

The polymer was synthesised according to a procedure described elsewhere [16].

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[*] Corresponding author. Present address: Los Alamos National Laboratory, CST-1 Advanced Chemical Diagnostics and Instrumentation, MS-J 565, Los Alamos, New Mexico 87545, USA.

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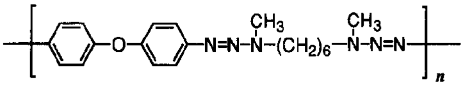

Scheme 1. Chemical structure of the triazenopolymer.

Thin films of variable thickness were prepared using the solvent cast technique with spectroscopic grade solvent (chloroform, Aldrich). The films were casted on quartz wafers of 5 cm diameter and 2.2 mm thickness. The homogeneity of the films was tested by recording the UV spectra at different positions of the wafer.

2.2. Instruments

Irradiations have been carried out using a Lambda Physics EMG 102 MSC excimer laser at 308 nm and a Lambda Physics EMG 201 MSC excimer laser at 248 nm. The energy was measured with a Gen-Tec joule meter, model ED 500. The UV spectrum were recorded on a Shimadzu UV 2100 spectrometer.

The sample transmission was measured using a Hamamatsu photo tube, type R 1193 U-95, which was equipped for the irradiation at 248 nm with an additional filter, Hamamatsu E 3331. As trigger, a Stanford Research System Instrument, model DG 535, four channel digital delay/pulse generator was used. The pulse was recorded with an Iwatsu TS 8123 storage scope which was connected with a RIKEN Denshi Co recorder.

3. Results and discussion

3.1. Threshold of ablation

The threshold fluence (F_{Th}) is used to quantify the ablation of the polymer. Normally, this value is calculated from a linear plot of the etch depth $d(F)$ versus ln F according to

$$d(F) = \frac{1}{\alpha_{\mathrm{eff}}} * \ln\left(\frac{F}{F_{\mathrm{Th}}}\right) \qquad (1)$$

where F = the laser fluence in mJ cm^{-2}. The effective absorption coefficient, α_{eff}, during ablation is calculated from the slope of these plots. With this method, the etch depth and energy are normally averaged over many pulses due to the pulse energy variation of the laser (up to 20%).

This variation is the reason why other investigations have applied a quartz micro balance (QMB) [17,18] technique to measure the threshold with a much higher precision.

As an alternative technique, conventional UV-spectroscopy is used in this study to determine the ablation threshold with single pulses. The absorbance of thin polymer films cast on quartz wafer were measured before and after irradiation with various fluences. For all of the measurements, only single pulses were used to exclude the influence of chemical (incubation) or physical (microstructures) changes due to successive pulses. The change of the absorbance at the maximum, ΔA, after irradiation was normalised for the different fluences, $\Delta A/F$, and averaged over 3–5 measurements. Figs. 1 and 2 show the change of the absorbance, $\Delta A/F$, as a function of laser fluence for 248 and 308 nm irradiation. The graphs are for film thicknesses of 0.21 μm and linear axes are chosen for a more detailed view of the changes.

The threshold fluence is defined as the fluence where a sudden increase of $\Delta A/F$ is observed. A closer inspection of the Figs. 1 and 2 shows that a different behaviour could be observed for 248 nm and 308 nm irradiation. The ablation at 308 nm, where the polymer has a higher absorption coeffi-

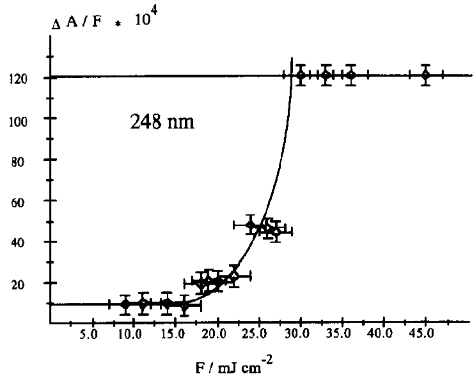

Fig. 1. Plots of the change of absorbance ΔA of thin polymer films (0.21 μm), recorded before and after single pulse irradiation with 248 nm. The values are normalized with the applied fluence and plotted versus the fluence. A nearby exponential increase is detected between 16 and 32 mJ cm^{-2}.

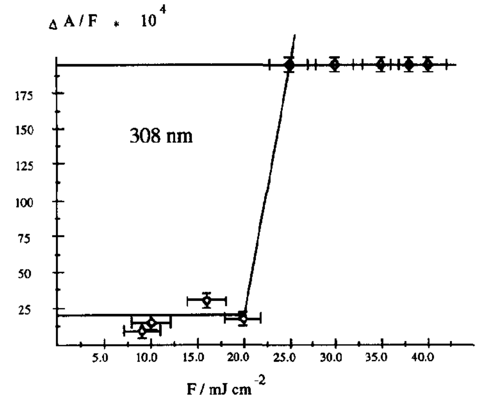

Fig. 2. Plots of the change of absorbance ΔA of thin polymer films (0.21 μm), recorded before and after single pulse irradiation with 248 nm. The values are normalized with the applied fluence and plotted versus the fluence. A sudden increase is detected between 20 and 25 mJ cm^{-2}.

cient ($\alpha_{\text{eff}} = 166000$ cm^{-1}), showed a very clear and well-defined threshold fluence. This kind of a sharp threshold, was previous only found for irradiation of polyimide (PI) with an ArF excimer laser (193 nm) [20] and assigned to a 'photochemical process'. In this study single pulse data were employed and the threshold was analyzed by using the QMB technique.

Contrary to the XeCl excimer laser irradiation the threshold at 248 nm ($\alpha_{\text{eff}} = 66000$ cm^{-1}) is not clearly defined. A description as a 'threshold fluence region' [19] is more appropriate. In the fluence range from 16 to 32 mJ cm^{-2} an increase of $\Delta A/F$ is detected, which might be described as exponential, followed by a linear area as shown in Fig. 3. In the case of polyimide (PI), such a broad threshold with an exponential increase was ascribed to a 'photothermal mechanism' [18].

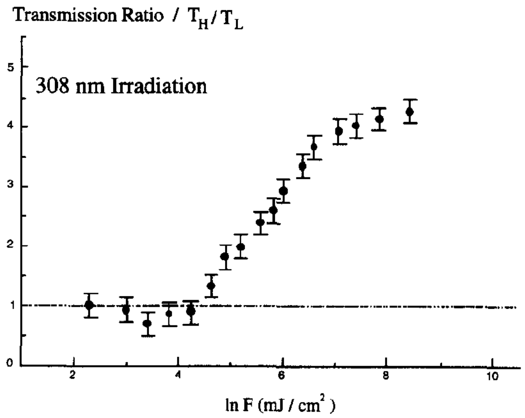

Fig. 3. Transmission ration (high fluence transmission/low fluence transmission) versus laser fluence at 308 nm. The discrete data points indicate the experimental results. The linear behaviour is indicated with the line at 1.

An explanation of the threshold behaviour which is assigned to photochemical or photothermal process is not possible only using the magnitude of α_{lin} or the photon energy of the laser. Therefore, the influence of material properties (quantum yield of photolysis, bond strength, etc.) and constants (thermal conductivity, reflectivity, decomposition temperature, etc.) must also be considered.

3.2. Transmission studies

The transmission of the laser pulse (T_H) was measured at various fluences. At each fluence, the pulse shape and height was averaged over ten to twenty pulses with a quartz wafer at the sample position. The fluence was adjusted by varying the sample position relative to the fixed positions of the lens and photo-tube. 5–10 films with various thicknesses (20–350 nm) were prepared, and each thickness was measured 2–4 times. The sample transmission was analysed using the simple peak amplitude because no large pulse distortions were detected and the use of the integral of the pulse did not alter the results. The low intensity value of transmission was measured for all films with a conventional UV spectrometer. This value is called T_L in agreement with Ref. [15] and plotted against the transmission of the laser pulse T_H. For each fluence the value T_H for a fixed film thickness of 0.1 μm was calculated from the linear plots of the film thickness versus T_H. An effect of internal reflection did not appear in the data. For all applied fluences linear relations between the used film thicknesses and the transmission values result. Therefore internal reflection is considered of minor influence.

The ratio of T_H/T_L as suggested by Pettit et al. [15] was plotted against the laser fluence. For 248 nm irradiation only fluence values up to about 800 mJ cm^{-2} could be used because at higher fluences (e.g. 1.1 J cm^{-2}) ablation of the quartz occurs. For

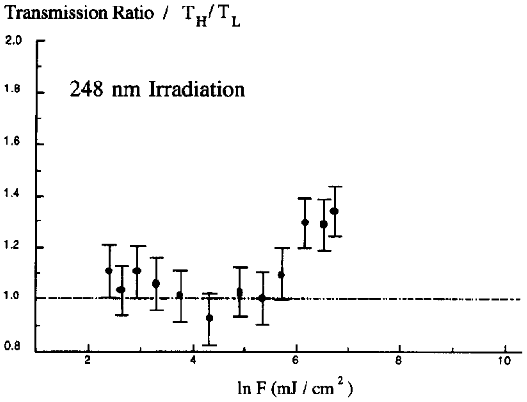

Fig. 4. Transmission ration (high fluence transmission/low fluence transmission) versus laser fluence at 248 nm. The discrete data points indicate the experimental results. The linear behaviour is indicated with the line at 1.

the same reason, the upper fluence limit for 308 nm irradiation is about 2.5 J cm^{-2}.

For the XeCl excimer laser irradiation, a clear increase of the transmission ratio starting at about 120 mJ cm^{-2} is observed (shown in Fig. 3). Whereas for 248 nm, only a slight increase is found (shown in Fig. 4) which is possible due to the limited fluence range.

The increase of the transmission ratio T_H/T_L at 308 nm exceeds the values at 248 nm, showing that the dynamic target optics could explain the experimental etch rates [11].

4. Conclusion

The study of the triazenopolymer using a conventional UV spectrometer showed a clearly defined threshold fluence at 308 nm, whereas with 248 nm irradiation a 'threshold fluence region' is determined.

The transmission for ns UV pulses is clearly dependent on the fluence in a range of some mJ cm^{-2} to several J cm^{-2} . With 248 nm irradiation, only a slight increase of the transmission ratio T_H/T_L could be detected, whereas with the XeCl excimer laser irradiation much higher transmission ratio values are reached which are close to the theoretical limit.

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